

First principles study of electronic transport through a Cu(111)|graphene junction

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We report first principles investigations of the nonequilibrium transport properties of a Cu(111)|graphene interface. The Cu(111) electrode is found to induce a transmission minimum (TM) located -0.68 eV below the Fermi level, a feature originating from the Cu-induced charge transfer resulting in n -type doped graphene with the Dirac point coinciding with the TM. An applied bias voltage shifts the n -graphene TM relative to the pure graphene TM and leads to a distinctive peak in the differential conductance indicating the doping level, a characteristic not observed in pure graphene.

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Since the discovery of graphene (Gr), much research, fueled by the advancement of scientific and technological progress at the nanoscale, has focused on the exceptional intrinsic electronic character of this two-dimensional material [1]. Within the context of nanoelectronics, utilizing Gr as an element in a device, e.g., electrode or channel, most likely requires interfacing it with other materials, a process known to potentially override/limit the unique properties of the Gr. In this view, recent experimental [2] and theoretical [3–6] studies have focused on the contact properties of Gr-based devices and how the presence of other materials can influence the global response of a device; a principle used to demonstrate a high-speed Gr photodetector [7]. Thus in regard to transport, a physical understanding of the Gr-metal contact, including the materials specific bonding, is paramount.

With the advent of large-scale epitaxially grown Gr on Cu [8], relatively straightforward fabrication of macroscopic Gr samples is possible, hence facilitating scientific and technological purposes. This advancement also highlights the current importance of Cu-Gr interaction. Whether etching part of the Cu substrate to realize a device or transferring Gr to another substrate, some degree of Cu may remain in contact with the Gr. Thus a clear understanding of the influence of Cu on the electronic and transport characteristics of Gr is advantageous.

In this paper, we present a nonequilibrium *ab initio* study of the transport properties of a Cu-Gr interface (as shown in Fig.1(a), hereafter referred to as Cu|Gr). Our findings show that a Cu electrode induces a transmission minimum (TM) located at -0.68 eV below the Fermi level (E_F), denoted as TM1, in addition to the TM of pure Gr at E_F (TM2), both due to a vanishing density of states (DOS) at the Dirac point. TM1 originates from a weak hybridization between Gr and Cu, which (i) preserves Gr's linear dispersion bands around the K point and (ii) induces a net charge transfer from

Cu to Gr resulting in n -type doped Gr (n -Gr) [3]. Applying a bias shifts the position of the TMs relative to each other, leading to a peak in the differential conductance (dI/dV) that is otherwise not observed in pure Gr.

The atomic coordinates of the Cu|Gr interface were optimized using VASP [9], a density functional theory (DFT) package. The nonequilibrium transport properties were calculated using MATDCAL [10], which combines nonequilibrium Green's functions (NEGF) with DFT to model open systems in a two-probe geometry. For MATDCAL, we use an optimized double- ζ polarized atomic basis set, the local density approximation for exchange-correlation energy [11], and norm-conserving non-local pseudopotentials [12] to account for the nuclear and core potentials. Converged k -meshes, including the important Γ , K and M points, were well tested and adopted in all calculations.

As illustrated in Fig.1(a) the left and right leads, extending to $\pm\infty$, are comprised of Cu-sandwiched Gr, simulating the situation where a metallic contact is deposited on Gr, and pure Gr, respectively. The system was chosen to replicate the interface between a source/drain region of a Gr device (Cu-coated Gr) and the pure Gr channel. Periodic boundary conditions are imposed in the plane perpendicular to transport. Figure 1(b) shows the atomic structure of the left lead of the Cu(111)|Gr interface. The most stable configuration of Gr on Cu(111) corresponds to one sub-lattice C atom situated directly above a Cu atom and the other C atom located at the hollow site of the Cu(111) surface [3]. The supercell of the left lead for total energy and electronic structure calculations is shown with the dotted box in Fig.1(b), where the images of the Gr sheets in neighboring supercells are separated by seven Cu(111) layers. By simultaneously relaxing the atomic coordinates to forces < 0.01 eV/Å and optimizing the supercell box size by total energy minimization, the Gr-Cu(111) interlayer distance is found to be 2.95 Å.

The band structure of the left lead is shown in Fig.1(c). The blue lines represent the hybrid states of the Cu-Gr contact, while the black circles show the p_z character of the C atoms corresponding to the Gr π -states. From this projection, we observe that the Gr bands conserve a lin-

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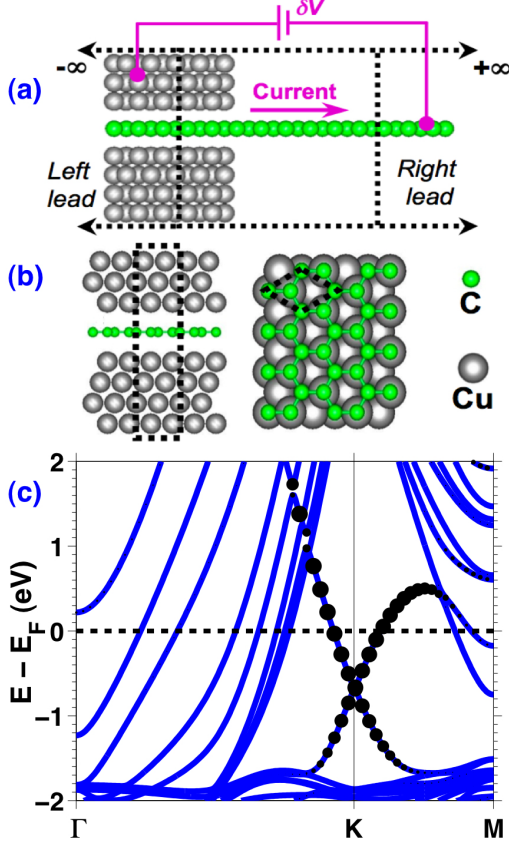


FIG. 1: (Color online) (a) Atomic structure of the Cu(111)|Gr interface. The black dotted lines delimit the scattering region from the left lead (Cu-contacted Gr) and right lead (pristine Gr) each extending to $\pm\infty$. (b) Side- and top-view of the left lead. The optimized distance between the Gr sheet and the Cu(111) surface is 2.95 Å. (c) Band structure of the left lead. The states originating from the hybrid Cu(111)|Gr system are plotted as solid blue lines, while the $C(p_z)$ character of the bands are superimposed as black circles. The dotted black lines, shown in (b), indicate the supercell box used for the electronic structure calculation.

ear dispersion near the K point, as previously shown for Gr in contact with one Cu(111) surface [3]. The weak hybridization between Gr and Cu merely shifts the conical Gr states down -0.68 eV relative to E_F resulting in n -type doped Gr. This energy shift in the Gr bands is somewhat larger than the value obtained for a single Cu(111) surface with the same interlayer distance [3].

Figure 2 shows the transmission coefficient (T) versus energy (E) as a function of Gr orientation at equilibrium ($V = 0$). A Gr sheet oriented such that transport occurs along the zigzag or armchair direction is denoted as Gr(zigzag) or Gr/armchair, respectively. The solid thick blue (thin red) line corresponds to the Cu|Gr(zigzag) (Cu|Gr/armchair) interface. A TM (i.e., TM2) is observed at E_F (E_F is shifted to zero), due to the vanishing density of states (DOS) in the pure Gr right lead. Interestingly, a second TM (i.e., TM1) is located at -0.68 eV.

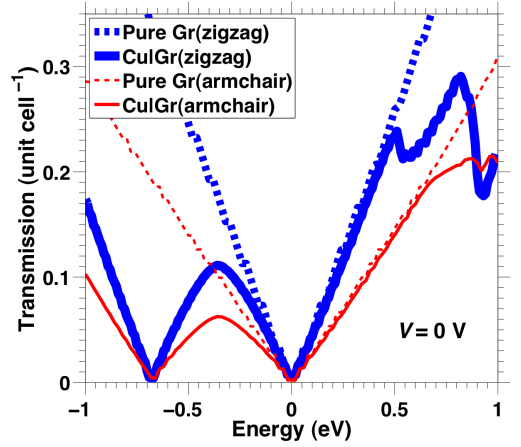


FIG. 2: (Color online) Transmission versus energy at equilibrium ($V = 0$ V) as a function of Gr orientation. The solid thick blue (thin red) line represents a Cu(111)|Gr interface where the Gr is oriented such that transport occurs along the zigzag (armchair) direction. The dashed thick blue (thin red) line shows the transmission for pure zigzag-oriented (armchair-oriented) Gr. The Fermi level is set to zero.

This feature also originates from the near-zero DOS at the neutrality point of the Cu-induced n -Gr in the left lead (see Fig.1(c)) [6]. This indicates that the many available metallic bands near the TMs, shown in the band structure, play a negligible role in the electron flow of the junction. To study the influence of the Cu electrode on the transport properties, we calculate T for pure Gr (dashed lines). We find that T near E_F is unaffected by the presence of the Cu electrode, while the same is also true near the TM1. This confirms that a Cu(111)|Gr interface can be effectively viewed as a n -Gr|Gr junction. Finally, we consider the effect of Gr orientation on T and conclude that both curves are related by a constant scaling factor. The ratio of $T_{\text{zigzag}}/T_{\text{armchair}}$ is found to be equal to the ratio $W_{\text{armchair}}/W_{\text{zigzag}}$, where W is the width of the supercell used for transport. Thus, T (and hence current) per unit width results in identical values for both zigzag and armchair orientations.

In Fig.3(a), we present T versus E as a function of applied bias (V) for Cu|Gr(zigzag). A bias V varies the chemical potentials of the left and right leads as $\mu_L = E_F$ and $\mu_R = E_F + |e|V$, where e is the electron charge. From Fig.3(a), we see that the TM1 is pinned at -0.68 eV (shown with the dashed vertical line), whereas the TM2 moves by an amount $|e|V$ (indicated by the arrows). This is easily understood because our bias is applied to the right Gr lead which shifts the Dirac point there. By applying a bias one can shift the relative positions of the TM features. From the T calculated at finite V , we obtain the current per unit width (I) for Cu|Gr(zigzag) and pure Gr(zigzag) shown in Fig.3(b). I is calculated

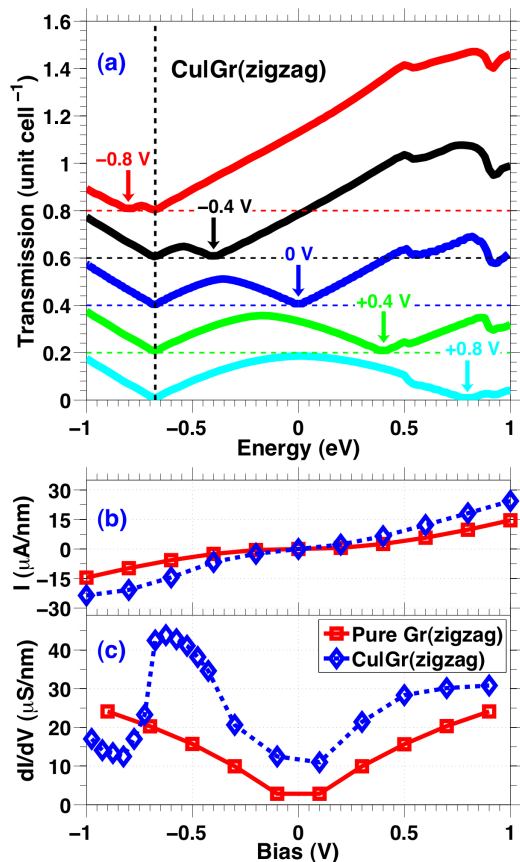


FIG. 3: (Color online) (a) Transmission versus energy as a function of applied bias V for the Cu(111)|Gr(zigzag) interface. The transmission curves corresponding to $V = +0.8$ V, $+0.4$ V, 0 V, -0.4 V, -0.8 V, are offset by 0, 0.2, 0.4, 0.6, 0.8 respectively, with the zero plotted as a dashed horizontal line. The arrows (black dashed vertical line) indicate the position of the Dirac point of the pure Gr right lead (n -type Gr left lead). Current I (b) and differential conductance dI/dV (c) per unit width versus V for Cu(111)|Gr(zigzag) and pure Gr(zigzag).

using the relation

$$I = \frac{2e}{hW} \int_{-\infty}^{+\infty} T(E, V) [f_L(E, \mu_R) - f_R(E, \mu_L)] dE \quad (1)$$

where h is Planck's constant, W the unit cell width and $f_{L,R}$ the Fermi-Dirac distribution functions. The I - V curves are smooth non-linear functions of V . To emphasize the differences between the Cu|Gr and pure Gr, we calculate the differential conductance per unit width $G \equiv dI/dV$, presented in Fig.3(c). Pure Gr results in a symmetric monotonic G , whereas Cu|Gr shows a peak near -0.63 V where both Dirac points from the Gr and n -Gr coincide in energy. For V greater than -0.63 V, the TM1 plays no role in the values of I and G , since it is out of range for the integration in Eq.(1) (from $E_F + |e|V$ to E_F , when $V < 0$ and temperature is zero). When $V < -0.63$ V, the TM1 enters the energy integration range for I and results in a rapid decrease in G . The maximum derivative of G provides the location of the conical point of the n -Gr. This prediction should be experimentally detectable.

In summary, we performed first principles transport studies of the Cu(111)|Gr interface. A Cu(111) electrode on Gr induces a second conductance minimum near -0.68 eV relative to E_F , originating from the vanishing density of states of the Cu-induced n -doped Gr. We find a Cu|Gr interface can be effectively modelled as a n -Gr|Gr junction due to a relatively weak interaction between Cu and Gr. An applied bias shifts the positions of the conductance minimums relative to each other, leading to a peak in the differential conductance (indicating the doping level of the n -Gr), a distinctive feature not observed in pure Gr. These results provide a general picture of the influence of weakly interacting metallic electrodes, including Al, Ag, Au and Pt [13], on transport in Gr.

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